

Analytical solution of CO₂ mass flux measurement with Non-Dispersive Infrared sensors for soil in diffusive and advective-diffusive regime: Tool for the continuous and telemetric measurement of volcanic gases in an open chamber

Solución analítica de la medida de flujo de CO₂ con sensores infrarrojos no dispersivos para suelo en régimen difusivo y advectivo-difusivo: herramienta para la medida continua y telemétrica de gases volcánicos en cámara abierta

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Abstract: Measuring the carbon dioxide (CO₂) mass flux in a volcanic environment is necessary for volcanic monitoring. CO₂ mass flux must be measured continuously and telemetrically to get, almost in real-time, a better understanding of the dynamics of the volcanic degassing processes, contributing to the building, together with other monitoring technics, of a volcano behavior model. This study presents two analytical solutions, 1) a simple diffuse solution and 2) an advective-diffusive solution, which both implement NDIR (Non-Dispersive Infrared Emitter) sensor arrays in an open chamber (diffusion chimney) and an exchange chamber (gas interchanger). The first system, for which the gas speed is negligible, despite being basic (with values reflected in the slope of an equation line), introduces mass flux calculations with a single sensor NDIR. For the second system, where the gas speed is part of the equation, another mathematical solution and three measuring points are required, which demands the system to include a second NDIR sensor for the correct mathematical solution of the equations system. In addition, an embedded system can automate the method by calibrating, controlling an agitation fan, and recording temperature, pressure, and mass flux in volcanic soils at the surface. Since this theoretically proposed method needs to be tested, experimental data are expected to validate the measurement of CO₂ mass flux, which will be used as a helpful tool for volcanic monitoring.

Keywords: Volcanic monitoring, volcanic activity diagnosis, embedded system, CO₂ mass flux.

Resumen: La medición del flujo de dióxido de carbono (CO₂) en un ambiente volcánico es una necesidad para el monitoreo volcánico. El flujo de CO₂ se debe medir de manera continua y telemétrica para una mejor comprensión, casi en tiempo real, de la dinámica de los procesos de desgasificación volcánica, que contribuyan a la construcción de un modelo de comportamiento volcánico, junto con otras técnicas de monitoreo. Este documento presenta dos soluciones analíticas, la

primera es una solución difusa simple y la segunda es la solución advectiva-difusiva, que implementan un arreglo de sensores NDIR (emisor de infrarrojo no dispersivo) en una cámara abierta (chimenea de difusión) y una cámara de intercambio (intercambiador de gases). El primer sistema, a pesar de ser básico (con valores reflejados en la pendiente de una línea de ecuación), y para el que la velocidad del gas es despreciable, permite introducir a expertos en este campo en los cálculos de flujo de este tipo con un solo sensor NDIR. Para el segundo sistema, donde la velocidad del gas es parte de la ecuación, se requiere otra solución matemática y tres puntos de medida, que exige la inclusión de un segundo sensor NDIR para la correcta solución matemática del sistema de ecuaciones. Un sistema embebido puede automatizar el método por calibración mediante el control de un ventilador de agitación, que registre la temperatura, la presión y la medición del flujo en suelos volcánicos en la superficie. Este método propuesto teóricamente necesita ser probado, por tanto se esperan aportes experimentales para validar la medida de flujo de CO₂ como una herramienta poderosa para el monitoreo volcánico.

Palabras clave: Monitoreo volcánico, diagnóstico de la actividad volcánica, sistema embebido, flujo de CO₂.

1. INTRODUCTION

The Earth emits gases, which are specific and possibly measurable as soil gas emissions in certain geological environments such as volcanic areas. Some gases are related to changes in the volcanic activity allowing its evaluation. Soil gas emissions have also been investigated in earthquake areas and along active fault zones (Allard et al., 1991; Badalamenti et al., 1988, 1991; Diliberto et al., 1993; Giammanco et al., 1998; Chiodini and Frondini, 2001; Gerlach et al., 2001; Ciotoli et al., 2003). Active volcanoes have been monitored periodically through the measurements of soil gas emissions because it is a good sign of change in their activity, and in many volcanic areas, there have been different projects in order to obtain accurate measurements for this purpose (Wakita, 1996; Ciotoli et al., 1998; Guerra and Lombardi, 2001; Rogie et al., 2001; Spicák and Horálek, 2001; Salazar et al., 2002).

According to Sahimi (1995), diffusion and advection result from the two different processes of the gas flux through natural soil. There are several ways to measure the CO₂ flux. One method, for example, is the calculation of the CO₂ flux from the concentration gradients in the soil (Baubron et al., 1990). In addition, it is possible to measure the absorption of CO₂ in a caustic solution, as in the alkali absorption method (Witkamp, 1966; Kirita, 1971; Anderson, 1973), or to measure the difference in CO₂ concentrations between the inlet and outlet air in a closed chamber, as in open flow infrared gas analysis (Witkamp and Frange, 1969; Nakadai et al., 1993).

In the dynamic concentration method (Gurrieri and Valenza, 1988; Giammanco et al., 1995), the measurement of the CO₂ content in a mixture of air and soil gas is obtained from a special probe. Gurrieri and Valenza (1988) deduced that the dynamic concentration is proportional to the soil CO₂ flux according to an empirical relationship. For example, Camarda et al. (2007) used the dynamic concentration technique in Vulcano, which belongs to the Aeolian Islands, in Italy.

Accurate measurement of CO₂ emission in a volcano's soil can be done with a "gas accumulation chamber" devise which consists of a noninvasive CO₂ concentration measurer (such as the NDIR method) and a known volume chamber placed on the soil surface. The gas accumulates in the chamber, and it is registered

using, for example, a West Systems instrument with a LICOR LI-800 Non-dispersive infrared CO₂ detector (Tonani and Miele, 1991; Bekku et al., 1955; Norman et al., 1992; Chiodini et al., 1998; West Systems, 2012). With the calculation of the accumulation slope with respect to the time and the system constants, it is possible to obtain the CO₂ mass flux from the sampled point. This technique, clearly manual and designed for research and monitoring (Hernández et al., 2001), needs complex automation for continuous and telemetric use to monitor a volcano status. The accumulation chamber technique has been used in volcanoes such as the Stromboli volcano (Inguaggiato et al., 2013), in the volcanic areas of Solfatara of Pozzuoli, and the Vesuvius volcano (Cardellini et al., 2003), all of these in Italy; El Chichón volcano in Mexico (Jácome et al., 2016); Mount Fuji volcano (Notsu et al., 2006) and Miyakejima volcano (Hernández et al., 2001), both in Japan.

On the other hand, some authors have mentioned open chamber measurement techniques (Janssens et al., 2000 and Camarda et al., 2007). However, they have not been popularized due to difficulties with wind impacts, pressure changes, and system size. This paper shows the analytical solution for the measurement of CO₂ mass flux, based on an open chamber (diffusion chimney (DC) in this paper) and an exchange chamber (gas interchanger (GI) in this paper). This study proposes a model to monitor the CO₂ mass flux in the soil for an active volcano, but it is also possible to use it for other purposes like agriculture. Furthermore, using one or two NDIR sensors capable of measuring CO₂ would make it possible to measure diffuse and advective-diffuse cases, respectively.

Using the newly proposed technique, a stations network could continuously measure CO₂ emitted at a specific volcano area per day. It could be validated with non-continuous and non-telemetric measurements, for instance, using the portable manual accumulation chamber instrument. This document proposes an analytical solution for this type of system. It takes advantage of the reduced number of mechanical parts required for their implementation, allowing an automatic and continuous measurement of CO₂ mass flux in volcanic soils.

The solution of a 3×3 equation system does not require knowledge of the soil characteristics that condition the speed of the gas that emerges due to advection-diffusion. The placement of two NDIR sensors inside the open chamber (diffusion chimney (DC) in this document) allows calculating this speed without affecting the CO₂ gradient. A new parameter called N will establish the state of the measurement system in a simplified way, defining the diffusive or advective-diffusive state and the inflection point. Additionally, new strategies are added in the design stage to minimize the difficulties already studied by other authors of the opened chamber techniques and to advance the alternative designs of continuous CO₂ mass flux measuring equipment for volcanic applications with an open chamber.

2. DEFINITIONS

Diffusion chimney (DC): The tube that connects the soil with the gas interchanger (GI). It allows mixing of the CO₂ gas that emerges from the ground with the atmosphere so that its concentration slowly decreases until it reaches the GI. Ideally, the soil emits a very high concentration of CO₂ gas and it decreases to reach the natural environmental concentration of the air through the DC and the GI (Camarda et al., 2007). As will be seen in the theoretical example defined by the new factor N (defined below), the transition from a diffusive to a diffusive-advective flow will be a value of approximately $1.47 \frac{\text{mg}}{\text{cm}^2 \cdot \text{s}}$ (see section 7.4).

Gas interchanger (GI): A tube system with a diameter bigger than the DC with ventilation holes. A homogeneous sample of the external gas is stored within the volume as a reference concentration well with or without external airflow. The tube at the bottom is in contact with the transmitting DC of CO₂.

NDIR: The CO₂ sensor under the Non-Dispersive Infrared Emitter (NDIR) technique, which obtains the concentration of CO₂ (ppm) in the DC in one position.

CO₂ mass flux: defined as $J_i(z, C) \left| \frac{\text{mg}}{\text{cm}^2 \cdot \text{s}} \right|$ is the mass of CO₂ per time unit and per area unit, calculated from a physicochemical model that integrates diffusion and advection. CO₂ mass flux is obtained by measuring the

CO₂ concentration using the NDIR sensors, recording their position within the DC, estimating the external reference concentration, and considering the system's constants and variables.

3. PRINCIPLES OF THE MEASUREMENT SYSTEM

The proposed system can detect CO₂ mass flux emissions by diffusion and advection by measuring the concentration of two NDIR sensors in a DC and the base level of environmental concentration of CO₂ in a GI. In low mass fluxes, the diffusion predominates and needs only one sensor. However, in high mass fluxes, the system is governed simultaneously by diffusion and advection (Gurrieri and Valenza, 1988) and requires the data of the two sensors.

3.1. Diffusion process

Each time there is a change of the CO₂ concentration in the soil, that is, the lower part of the DC, a diffusion process occurs between two gases (gas coming from the soil and gas in the air), reflected in mass flux (García, 2020). This air with a higher CO₂ concentration (higher molecular weight) occupies spaces in the upper air of the DC, where one of the CO₂ sensors is located (upper NDIR sensor), gradually reaching the external equilibrium concentration measure reference through the GI.

The above-mentioned process has two analyses: Stationary:

If the CO₂ emission is without variations in time, the diffusion will enter a stationary state. Removing the time variable from the system makes it possible to obtain the constant CO₂ mass flux.

Temporary: If the phenomenon's behavior is studied from the temporal point of view, it is possible to determine the linear measurements of the system's DC and the GI, adjusting it to the required sensitivity. Similarly, it is possible to get the response time of the system.

The above two analyses will be performed according to 1st and 2nd Fick's law, respectively, based on the mass transport phenomenon where no chemical reaction occurs within the physical kinetics of gases.

3.2. Advection process

When there is a significant change of pressure in the soil relative to the ambient air, the process of advection, also reflected in mass flux, is generated along with a diffusion process in the DC (Camarda et al., 2007). This process twists the diffusion line of the system, which requires an additional NDIR sensor (NDIR soil sensor) to solve the new system mathematically.

The above also has two analyses:

Stationary: If the CO₂ emission is without variations in time, it will have a behavior where the diffusion and advection enter a stationary state. Removing the time variable from the system makes it possible to obtain the constant CO₂ mass flux.

Temporary: If the phenomenon's behavior is studied from the temporal point of view, it is possible to determine the linear measurements of the system's DC and GI, adjusting it to the required sensitivity. Similarly, it is possible to obtain the response time of the system.

3.3. Advection-diffusion process

The mathematical model of the CO₂ mass flux meter is performed under the following laws and principles (Camarda et al., 2007):

For diffusion, according to Fick's 1st and 2nd laws.

For advection, according to Darcy's law.

The principle of mass conservation will be applied.

It will be considered that no chemical reaction occurs within the physical kinetics of gases.

4. THEORY

4.1. Diffusion

Diffusion is a phenomenon studied by physical chemistry, where systems that are not in equilibrium evolve to states, either chemically or physically, until reaching a new equilibrium (García, 2018). For this case, we will assume only the evolution to a physically stable state, where the thermodynamic variable of our system out of balance, can be described as in equation 1:

$$C_i = C_i(\vec{r}, t) \quad (1)$$

where:

C_i is the thermodynamic variable of the concentration of CO₂, and for this document, unless otherwise stated, the concentration shall always refer to CO₂.

\vec{r} is the position vector of the study concentration.

t is the time.

In 1855 Adolf Fick set two laws regarding the diffusion of two substances, which can be applied while the following conditions are satisfied:

The substances are at the same pressure.

The substances are at the same temperature.

The substances do not react chemically to each other.

A change in atmospheric pressure generates a mass current in the system, which must be measured by a pressure differential meter. Small changes in atmospheric pressure (~ 1 hPa) can generate large errors by increasing or underestimating the CO₂ mass flux. What happens is that the atmospheric pressure works like a pump that injects or sucks gas into the ground, directly affecting the mass flux measurement. With the inclusion of advection in the next section, we will see that this problem is solved with the calculation of the mass flux velocity and that the use of a differential pressure meter in the DC could correct this error in the instantaneous mass flux measurement.

Assume two containers that have a mixture of two substances A and B, with different concentrations of CO₂ at the same temperature T , and pressure P (see Figure 1.)

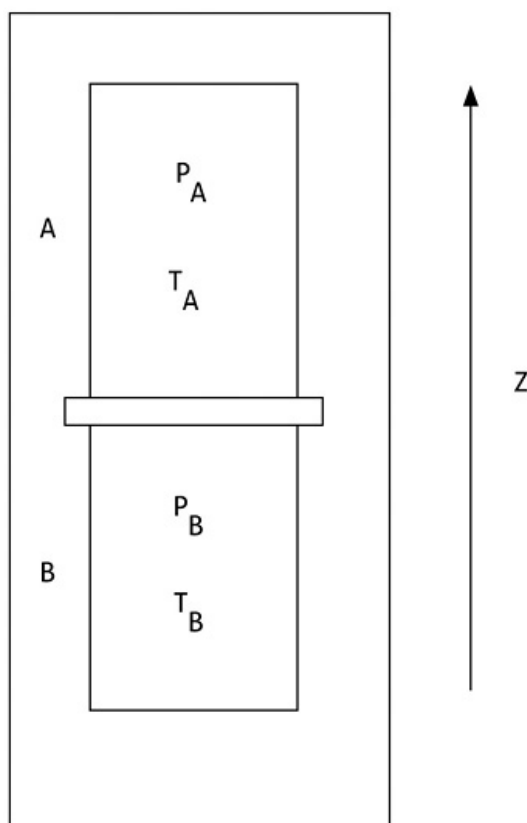


FIGURE 1
One-dimensional diffusion between two gases

The two substances are separated by an impermeable wall, which in an instant $t = 0$ is detached to allow the diffusion of the substance with the highest concentration B within the substance with the lowest concentration A. Thus, the molecular movement deletes the differences in concentration between the two substances, and this spontaneous decrease in concentration differences is called diffusion.

If the variable concentration is defined as C and the subscript A and B as indicators of the substance A and B, then C_A and C_B in the distance z change with the function of time. In Figure 2, C_A is equal to C_B after a certain amount of time ($t = \infty$). The Z -axis has been arranged horizontally for explanation.

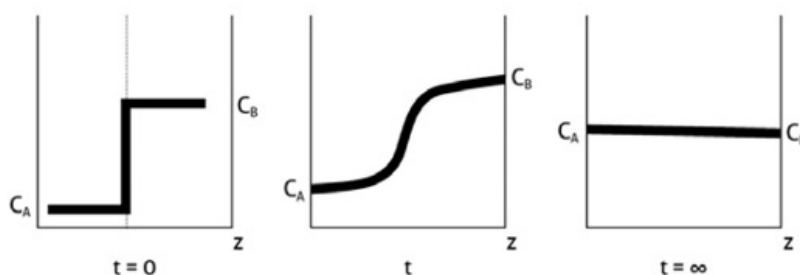


FIGURE 2.
Diffusion without stable wells in the boundaries
(Left) State for $t = 0$. (Center) Any value for $0 < t < \infty$. (Right) $t = \infty$

Diffusion is a macroscopic movement of the system's components due to the concentration gradient. In the proposed system, this diffusion disappears when the concentration differences are canceled, indicating that the system has reached equilibrium. If the concentration differences are kept within limits, they could reach a stationary state as in Figure 3.

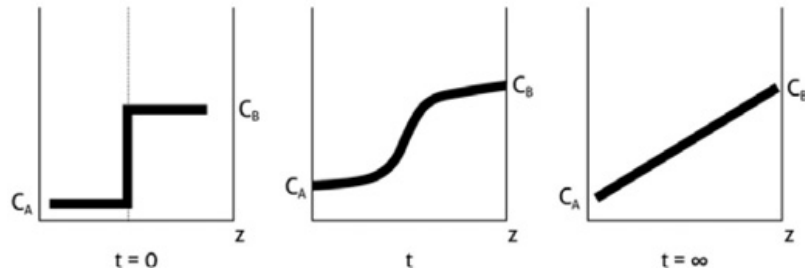


FIGURE 3

Diffusion with stable wells in the boundaries

(Left) State for $t = 0$. (Center) Any value for $0 < t < \infty$. (Right) $t = \infty$

This new model would be achieved when the two boundaries are stable wells of A and B substances concentration in the study, allowing that at $t = \infty$ a stationary state occurs in the concentration at any point.

4.1.1. Fick's first law

Fick's first law applies to determine stationary behaviors of diffusion, and it states that the mass flux through a plane between two adjacent systems is proportional to the concentration gradient and unidimensionally is written as (Camarda et al., 2007):

$$J_{dif} = -D \frac{dC_i}{dz} \quad (2)$$

Where:

D is the diffusion coefficient in $\frac{m^2}{s}$. Note: D will be equal to air inwards CO₂ as from CO₂ to air for practical purposes.

C_i is the concentration in $\frac{mg}{m^3}$; therefore, the [ppm] unit must be converted.

J_{dif} is the mass flux per diffusion at that point in $\frac{mg}{m^2 \cdot s}$.

The value of D according to the conditions of pressure and temperature of the site different from T₀ = 273.2°K(0°C) and P₀ = 1013hPa is obtained from the following formula with D(STP) = 1.39 × 10⁻⁵ $\frac{m^2}{s}$ (Campbell, 1985):

$$D = D_{(STP)} \left(\frac{T}{T_0} \right)^{1.75} \left(\frac{P_0}{P} \right) \left[\frac{m^2}{s} \right] \quad (3)$$

Where:

D(STP) is the diffusion coefficient in pressure and temperature standard conditions.

4.1.2. Fick's second law

Fick's second law applies to determine the temporal behaviors of diffusion and is written as García (2020):

$$\frac{dC_i}{dt} = D \frac{d^2C_i}{dz^2} \quad (4)$$

Where:

D is the diffusion coefficient in $\frac{m^2}{s}$ and does not depend on either C_i or z.

C_i is the concentration in $\frac{mg}{m^3}$.

Because Fick's second law can determine the temporal behavior, this allows knowing the system's response time to a change of mass flux in a non-stationary state.

Equation 4 is a differential equation with infinite solutions, but one solution applies boundary solutions and can be adjusted to our problem (Busquets, 2011):

$$\frac{C_s - C_0}{C_s - C_0} = 1 - \text{ferr}\left(\frac{z}{2\sqrt{D \times t}}\right) \quad (5)$$

Where:

ferr() is the error function of Gauss (Callister, 1995).

Cz is the concentration given by the sensor in [ppm].

C0 is the reference concentration in [ppm].

Cs is the concentration in the boundary in [ppm].

z is the distance to the point of interest in [m].

D is the diffusion coefficient in $\frac{\text{m}^2}{\text{s}}$.

t, is the time in [s].

4.2. ADVECTION

Advection is the variation of a scalar property at a given point, such as pressure or temperature, by a vector field effect. Here, the advection process will be defined by the pressure gradient #P that generates a mass transport process (Camarda et al., 2006, 2007).

4.2.1. Darcy's law

In 1856 Henry Darcy published the formula that bears his name and is currently called Darcy's law, which defines how to measure this type of advective mass transport (Camarda et al., 2006, 2007). Darcy's law determines the velocity of a fluid as a function of pressure gradient:

$$v = -\frac{k}{\mu} \nabla P \quad (6)$$

Where:

v is the gas velocity in $\frac{\text{m}}{\text{s}}$.

k is the intrinsic permeability, which is the only function of the soil properties in [m²].

μ is the gas dynamic viscosity in [Pa × s].

#P is the pressure gradient in $\frac{\text{Pa}}{\text{m}}$.

As seen below, it will not be from this equation that v will be calculated to determine the CO₂ mass flux, but the analytical solution with the advantage of using two NDIR sensors. The mass flux due to advection is obtained knowing the concentration and speed:

$$J_{adv} = C_i v \quad (7)$$

Where:

Ci is the concentration in $\frac{\text{mg}}{\text{m}^3}$.

v is the gas speed in the diffusion chimney in $\frac{\text{m}}{\text{s}}$.

Jadn is the mass flux per advection at that point in $\frac{\text{mg}}{\text{cm}^2 \cdot \text{s}}$.

4.3. ADVECTIVE-DIFFUSION THEORY

The simultaneous diffusion and advection processes are defined as the sum of the two mass fluxes acting simultaneously (Gurrieri and Valenza, 1988; Sahimi, 1995):

$$J_i = J_{dif} + J_{adv} \quad (8)$$

Using the definitions of equations 2 and 7, the mass fluxes remain as:

$$J_i = -D \frac{dC_i}{dz} + C_i v \quad (9)$$

The law of mass conservation must be considered to quantitatively describe a system where diffusion and advection occur simultaneously.

$$\nabla \cdot J_i + \frac{\partial C_i}{\partial t} = 0 \quad (10)$$

Where $\nabla \cdot J_i$ is the mass flux divergence J_i . By combining equations 9 and 10 and assuming that v and D are constant, the next equation is found:

$$v \nabla C_i - D \nabla^2 C_i = \frac{\partial C_i}{\partial t} \quad (11)$$

This is the equation for all problems where diffusion and advection are simultaneously involved. The one-dimensional equation to be applied to the DC would be:

$$v \frac{\partial C_i}{\partial z} - D \frac{\partial^2 C_i}{\partial z^2} = \frac{\partial C_i}{\partial t} \quad (12)$$

And in a stationary state:

$$v \frac{\partial C_i}{\partial z} - D \frac{\partial^2 C_i}{\partial z^2} = 0 \quad (13)$$

Which has a general solution (Isachenko et al., 1980):

$$C(z) = A \frac{D}{v} e^{\frac{v}{D} z} + B \quad (14)$$

Where A and B are constants that depend on the boundary conditions.

If this solution is tested to the two points model of concentration measurement, it is found that equations will be missing because apart from A and B , the value of v is also unknown. For this reason, it is necessary to place another NDIR sensor to have three equations and solve the three variables of the system (see section 5.3. Equation's approach).

5. MASS FLUX METER OF CO₂ BY ADVECTION AND DIFFUSION

The CO₂ mass flux meter of CO₂ by diffusion and advection proposed in this study works with two coupled chambers where diffusion and advection occur in the DC. Also, in the GI, a rapid diffusion occurs with the atmospheric air. The advection product of the pressure gradient has significant effects for velocities v , which are greater than a numerical tenth of D , that is, $v > \frac{D}{10}$ for a normalized diffusion chimney $z = -1$.

5.1. CONSIDERATIONS

In the DC, the measurement is performed with two CO₂ sensors. In general, the DC is long, narrow, and has a much smaller volume than the GI.

The GI works as a reference well for the wind filter and external atmospheric concentration, allowing the diffusion to operate in quiet and isolated from the outside. In general, the GI is short, wide, and has a much larger volume than the DC.

Due to the dimensions and openings of the DC and GI, the system:

Can be at the same temperature everywhere.

There may be a pressure gradient that generates a mass flux, deforming the concentration distribution into the DC.

Equally, it is assumed that:

GI is bigger than DC.

There is no chemical reaction between the gases emitted by the soil and air.

A sensor is as close as possible to the ground on the DC and will be called a soil sensor.

A sensor is at the upper side and is generally one-third of the length of the DC measured from above. This sensor will be called the upper sensor.

The upper sensor arrangement in a third of the effective length is called the cubic solution position; the quadratic solution position is set when the sensor is placed in the middle of the tube. This last solution position, although also valid, has little dynamic range as it will look mathematically.

5.2. THE N PARAMETER AND THE POSSIBLE STATES OF THE SYSTEM

On the way through the DC from the soil sensor to the atmospheric air (CO₂ concentration reference), a diffusive process occurs simultaneously, as there is a difference in concentration between the two points, and a diffusion-advection process can happen if there is simultaneously a significant pressure gradient. In this way, the DC and the GI will work as follows, generally for $z = -1$ (normalized to one meter), and the classification parameter N is defined as:

$$N = - \frac{D}{10 \times v \times z} \quad (15)$$

Which determines the status of the measurement system and is important to know whether the system is in a diffusive or advective-diffusive state.

The numerical simulation of equation 9 with the solutions of equation 14 for different system states provides interesting graphs interpreting the CO₂ concentration distribution along with the DC and the N parameter interpretation. These graphs are obtained for hypothetical speeds and solving only the unknowns A and B in a system of two equations with two variables knowing speed v . In sections 5.3. and 6.2. show the approach and solution of the equations that already consider the velocity v for an analytical solution that completes the system.

Possible states of the system, changing v and its relationship with the N parameter:

Without diffusion and advection ($N \gg 1$, $v @ 0$, $z = -1$): when there is no difference in the CO₂ concentration between the ends of the DC, the limits of which are the air near the ground and the GI, there will not be a gradient triggering the movement of any molecules. Inside the GI will have a reference concentration given by the atmosphere. Therefore, at any time, the two NDIR CO₂ sensors will have a concentration in ppm of the same proportion. If there is no less likely diffusion, there will be the advection

resulting from a large pressure gradient between the ground air and the atmospheric air. Figure 4 shows an illustrative graph where the two lines have been separated for demonstrative purposes.

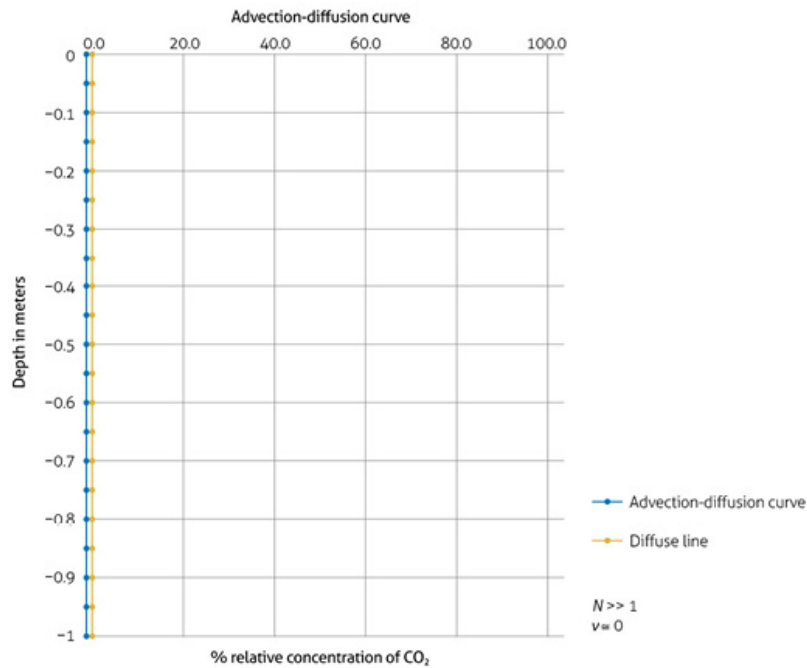


FIGURE 4
CO₂ percentage concentration with respect to depth for $v @ 0$

With diffusion and without advection ($+\infty > N > 1$, $0 < v < \frac{D}{10v_0}$, $z = -1$): when there is a CO₂ concentration difference between the ends of the DC whose limits are the soil and the GI, there will be a gradient that will mobilize CO₂. Inside the GI will have a reference concentration given by the atmosphere. At $t > 0$, with the system's characteristics and under a continuous emission of CO₂, the CO₂ NDIR sensors located inside the DC will record concentration changes. The difference in concentration in two environments works as a diffuser element of CO₂ (denser) to normal air (less dense), and the difference in this concentration between the soil sensor, the upper sensor, and the reference concentration given by the atmosphere is the essence of the mass flux meter. The point of $v = \frac{D}{10v_0}$ was chosen so that the error difference between the only diffusive and the advective-diffusive models would be a maximum of 1%. See Figure 5.

With diffusion and advection ($1 \geq N > 0$, $v \geq \frac{D}{10v_0}$, $z = -1$): when there is a significant pressure gradient of CO₂ between the air near the ground and the atmosphere, there will be a CO₂ mass flux between the DC and GI. This new mass flux is more significant than the CO₂ mass flux by diffusion. The effect on the diffusion line is to bend it upwards with a peak of about one-third relative to the diffusion line. This match allows for a higher dynamic range of the system in the upper sensor, significantly decreasing system errors. The value of $N = 1$ or $v = \frac{D}{10v_0}$ is called diffusion to advection-diffusion transition and is the point that corresponds to a maximum error of 1% compared to a linear model using Fick's first law. Figures 6a and 6b show the case of $0 < N \leq 1$, $v > \frac{D}{10v_0}$ and $N @ 0$, $v > \frac{D}{10v_0}$.

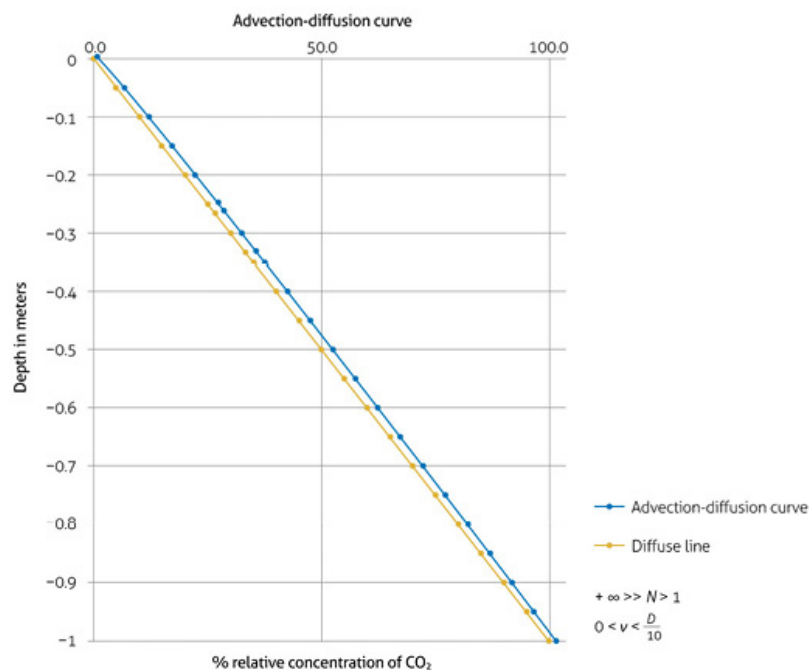


FIGURE 5

CO₂ percentage concentration with respect to depth for $+\infty \gg N > 1$, $0 < v <$

In summary, the performance of the system is based on the fact that a gas exposed to another is mixed evenly due to its intrinsic gas movement (diffusion) and also simultaneously by a pressure gradient that generates a velocity v (advection). The value of N determines:

$N \gg 1$, there is almost no mass flux by diffusion.

$N > 1$, is only diffusive.

$N = 1$, it has an advective-diffusive transition.

$1 > N > 0$ is advective-diffusive.

Two NDIR sensors at two points in the DC are required to perform the CO₂ mass flux measurement and thus solve the equations for the two diffusive and advective phenomena within the physical kinematics of the gases.

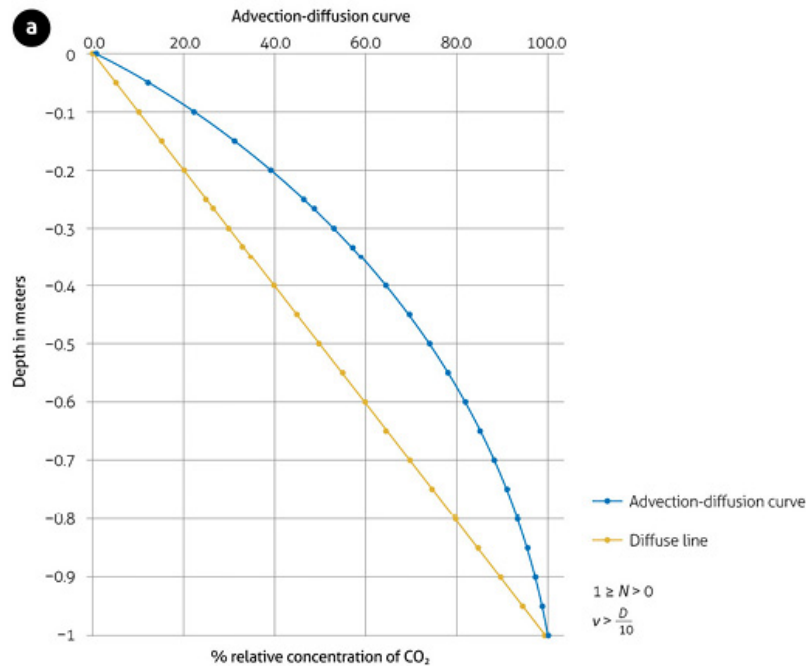


FIGURE 6. A)
CO₂ percentage concentration with respect to depth for $1 \geq N > 0$, $v > \frac{D}{10}$

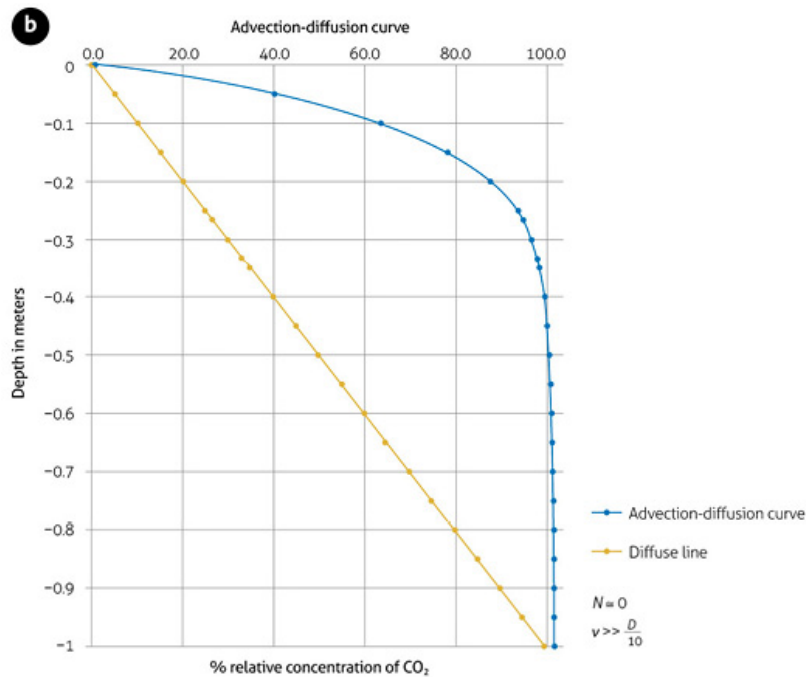


FIGURE 6 B)
CO₂ percentage concentration with respect to depth for $N \approx 0$, $v \gg \frac{D}{10}$

5.3. EQUATION'S APPROACH

The approach of equation 14 in three points of the diffusion chimney allows to solve A, B, and v , and hence to find the J_i mass flux as a function of three concentrations C_{Soil} , C_{Upper} , $C_{\text{Environment}}$ and the constant parameters D , z_0 , z_a , z_b . For an easier understanding, the next notation is defined:

$z = z_0 = 0$: Position at the top edge of the diffusion chimney.

$z = z_a$: Position in the upper third of the diffusion chimney (or in the middle).

$z = z_b$: Position in the soil of the diffusion chimney.

$C(z = z_0) = C_0 = C_{\text{Environment}}$: Example of environmental reference concentration 404ppm (for 2017) for this document (WMO, 2019).

$C(z = z_a) = C_a = C_{\text{Upper}}$: is the concentration at the point z_a .

$C(z = z_b) = C_b = C_{\text{Soil}}$: is the concentration at the point z_b .


Note 1: Each concentration given in ppm must be converted to $\mu\text{mol mol}^{-1}$, so the CO₂ measurements given by the NDIR sensors must be converted according to pressure and operating temperature.

Note 2: For all calculations, the coordinates axis will be positive upwards from the ground.

The detailed solution of this system can be found in the analytical solution in section 11.1. and have as a purpose two solutions: $z_b = 2 \times z_a$ and $z_b = 3 \times z_a$. The first is called a quadratic solution, and it is not practical because it limits the dynamic range. The second is called a cubic solution and fits well to the dynamic range due to the displacement of the concentration curve to the DC's upper third by the effect of the gas speed for $1 > N > 0$.

Figure 7 will be the reference for all explanations of the hypothetical assembly of the system for the CO₂ measurement in the other sections. In the case of $v = 0$, only the upper sensor shall be considered.

Table 1. Table of the physical model, boundary conditions, and equation 16

Diffusion chimney (DC)		Boundary conditions	Mathematical equation
	$z_0 = 0$ $C_0 = 404$	<ul style="list-style-type: none"> $z = z_0 = 0$: Position at the upper edge of the diffusion chimney. $C(z = z_0) = C_0$ $C_0 = C_{\text{Environment}} = 404\text{ppm}$ Example of environmental concentration reference. 	$C(z = z_0 = 0) = A \frac{D}{v} + B = C_0 = 404 \quad (16.1)$
	z_a, C_a	<ul style="list-style-type: none"> $z = z_a$: Position in the upper third of the chimney diffusion (or in the middle). $C(z = z_a) = C_a$ $C_a = C_{\text{Upper}}$ Is the concentration at the point z_a. 	$C(z = z_a) = A \frac{D}{v} e^{\frac{v}{D} z_a} + B = C_a \quad (16.2)$
	z_b, C_b	<ul style="list-style-type: none"> $z = z_b$: Position in the soil of the diffusion chimney. $C(z = z_b) = C_b$ $C_b = C_{\text{Soil}}$ Is the concentration at the point z_b. 	$C(z = z_b) = A \frac{D}{v} e^{\frac{v}{D} z_b} + B = C_b \quad (16.3)$

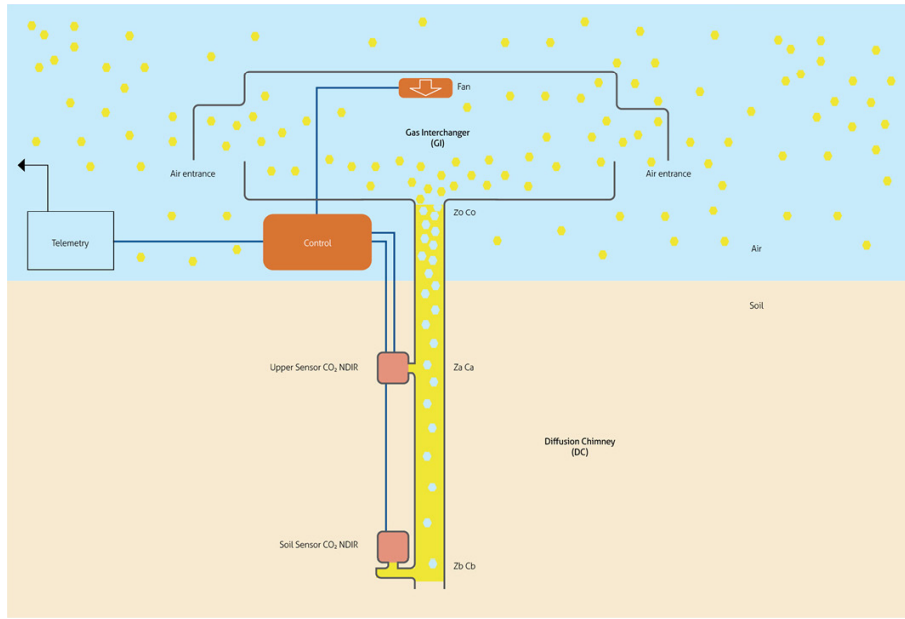


FIGURE 7.
Assembly of a prototype embedded system for the
measurement of CO₂ mass flux by diffusion and advection

6. MASS FLUX CALCULATION

6.1. THE SOLUTION FOR $v = 0$

The calculation of the J_i mass flux for $v = 0$ is obtained by integrating equation 2 (Fick's first law), and for the point $z = z_a$ and the concentration C_a , it will be:

$$J_i(z, C) = \frac{-D(C_a - C_0)}{z} \left[\frac{mg}{s \times m^2} \right] \quad (17)$$

6.2. THE SOLUTION FOR $v \neq 0$

The calculation of the J_i mass flux for $v \neq 0$ is determined by equation 9 with the solutions of equation 14 (see analytical solution number 11.1.2). After replacing the terms A, B, and v and simplifying, J_i will be as follows:

$$J_i = B \times v \left[\frac{mg}{s \times m^2} \right] \quad (18)$$

Where v is obtained from:

$$v = \frac{\ln(Y) \times D}{z_a} \quad (19)$$

And where Y is:

$$Y = \frac{-1 + \sqrt{1 - 4 \times \left(1 - \frac{(C_b - C_0)}{(C_a - C_0)} \right)}}{2} \quad (20)$$

Where:

$$C_b > C_a > C_0$$

$z_b = 3 \times z_a$ (is the cubic solution, see the analytic solution in 11.1.2)

The value of B is obtained as follows:

$$B = C_0 - \left(\frac{(C_a - C_0)}{\left(e^{\frac{\nu}{D} \times z_a} - 1 \right)} \right) \quad (21)$$

This means that it is only necessary to know C_b , C_a , C_0 , D , and z_a to get A , B , and ν , and thus obtain the J_i mass flux as long as it is satisfied that $C_b > C_a > C_0$ and $z_b = 3 \times z_a$.

7. THEORETICAL EXAMPLE

Suppose there is a diffusion chimney one inch in diameter and one meter long with a gas interchanger large enough to retain at its top a stable environmental concentration independent of the wind. There are two CO₂ concentration sensors, one at ground level at 1 m and the other at 0.333 m from the end of the chimney inwards. The system runs at 4,600 masl (Pressure 566 hPa), and the air temperature is almost constant at 10°C. Sensors after 45 minutes show the next concentrations at three different hours in the day: Measure 1: $C_a = 1,941.1$ ppm and $C_b = 5,000$ ppm; Measure 2: $C_a = 17,490$ ppm and $C_b = 50,000$ ppm; Measure 3: $C_a = 22,644.8$ ppm and $C_b = 50,000$ ppm. Assume $C_0 = 404$ ppm as the reference concentration at $T = 25^\circ\text{C}$ and $P = 1,013$ hPa; no adjustments are made for changes in atmospheric pressure, and it is recalled that length measurements are negative.

Questions:

- How much mass flux in $\frac{\text{kg}}{\text{m}^2 \cdot \text{s}}$ is being emitted for the measurements 1, 2, 3?
- Determine for measurements 1, 2, and 3 if the system is diffusive or advective-diffusive.

Data:

The 1-inch diameter data does not affect the measurement.

$z_a = -0.333$ m.

TABLE 2.
Table 2. Measurement

	Measurement 1	Measurement 2	Measurement 3
C_0	404 ppm	404 ppm	404 ppm
C_a	1,941.1 ppm	17,490 ppm	22,644.8 ppm
C_b	5,000 ppm	50,000 ppm	50,000 ppm

a) To calculate the mass flux, all values in ppm (the three measurements and points) should be changed to Importar imagen and adjusted for 4,600 masl and 10°C. Then the diffusion coefficient is calculated at the operating pressure and temperature. The mass flux velocity is then calculated using equations 20 and 19. The mass flux is calculated by equations 18 and 21.

b) To determine whether the system is diffusive or advective-diffusive for all three cases, it is necessary to evaluate the velocity ν obtained for the three cases and compare it with D by equation 15.

In the next sections, a step-by-step process is developed.

7.1. CALCULATION FROM PPM TO MG/M³ UNIT

To convert the concentration C given in ppm to $\frac{mg}{m^3}$, it is necessary to multiply the ppm (ratio of CO₂ molecules to total molecules in one volume) by the molecular weight of CO₂ and divide it by the number of moles that fit in that volume according to the law of gases $V = \frac{R \times T}{P}$.

But since the system also works at a different pressure and temperature, the concentration C given in ppm should be passed to the concentration C given in $\frac{mg}{m^3}$ referenced to $P = 1,013$ hPa and temperature $T = 25^\circ\text{C}$.

$$C \frac{mg}{m^3} = \frac{Mw_{CO_2} \times C_{PPM}}{\frac{R \times T}{P}} \times 10^{-1} \left[\frac{mg}{m^3} \right]$$

$$C \frac{mg}{m^3} = \frac{P \times Mw_{CO_2} \times C_{PPM}}{R \times T} \times 10^{-1} \left[\frac{mg}{m^3} \right] \quad (22)$$

Where

$C \frac{mg}{m^3}$ is the concentration given in $\frac{mg}{m^3}$.

P is the pressure in [hPa].

Mw_{CO_2} is the CO₂ molecular weight in $\frac{g}{mol}$ (according to the periodic table 44.01).

$CPPM$ is the concentration given in ppm by the NDIR sensor.

R is the constant of the ideal gases that equals 8.315684 in $\frac{J}{K \times mol}$.

T is the temperature in Kelvin degrees [$^\circ\text{K}$]. (Sum 273.2 to the value in $^\circ\text{C}$ to get $^\circ\text{K}$).

10^{-1} is the conversion factor of passing hPascals to Pascals, ppm to real value, and grams to milligrams:

$$10^{-1} = \frac{100 \text{ Pa}}{1 \text{ hPa}} \times 10^{-6} \times \frac{1,000 \text{ mg}}{1 \text{ g}}$$

For example, replacing $CPPM = 5,000$ ppm, $P = 566$ hPascals (4,600 masl), and 10°C the next result is obtained:

$$C \frac{mg}{m^3} = \frac{566 \times 44.01 \times 5,000}{8.315684 \times (273.2^\circ + 10^\circ)} \times 10^{-1} \left[\frac{mg}{m^3} \right]$$

$$C \frac{mg}{m^3} = 5,288.66 \left[\frac{mg}{m^3} \right]$$

Performing the calculations of the other values from ppm to $\frac{mg}{m^3}$ with pressure and temperature adjustment:

Table 3. Results

	Measurement 1	Measurement 2	Measurement 3
C_o	404 ppm-> 427.32 $\left[\frac{mg}{m^3} \right]$	404 ppm-> 427.32 $\left[\frac{mg}{m^3} \right]$	404 ppm-> 427.32 $\left[\frac{mg}{m^3} \right]$
C_a	1,941.1 ppm-> 2,053.18 $\left[\frac{mg}{m^3} \right]$	17,490 ppm-> 18,499.7 $\left[\frac{mg}{m^3} \right]$	22,644.8 ppm-> 23,952 $\left[\frac{mg}{m^3} \right]$
C_b	5,000 ppm-> 5,288.66 $\left[\frac{mg}{m^3} \right]$	50,000 ppm-> 52,886 $\left[\frac{mg}{m^3} \right]$	50,000 ppm-> 52,886.6 $\left[\frac{mg}{m^3} \right]$

7.2. VELOCITY CALCULATION

Then equations 19 and 20 are used to calculate the velocity of the gas. To determine measurement 1, the Table 3 values are used, then:

$$Y = \frac{-1 + \sqrt{1 - 4 \times \left(1 - \frac{(C_b - C_0)}{(C_a - C_0)}\right)}}{2} \quad (20)$$

$$v = \frac{\ln(Y) \times D}{z_a} \quad (19)$$

Replacing for measurement 1 in equation 20:

$$Y = \frac{-1 + \sqrt{1 - 4 \times \left(\frac{(5,288.66 - 427.32)}{(2,053.18 - 427.32)}\right)}}{2}$$

$$Y = 0.99666677$$

Replacing for the measurement 1 in equation 19 with the value of D adjusted to the pressure and temperature according to equation 3:

$$v = \frac{\ln(0.99666677) \times 2.66 \times 10^{-5}}{-0.333}$$

$$v = 2.66 \times 10^{-7} \left[\frac{m}{s} \right]$$

For the other measurements, see the following table:

Table 4. Results

	Measurement 1	Measurement 2	Measurement 3
Velocity	$2.66 \times 10^{-7} \left[\frac{m}{s} \right]$	$2.66 \times 10^{-6} \left[\frac{m}{s} \right]$	$2.66 \times 10^{-5} \left[\frac{m}{s} \right]$

7.3. MASS FLUX CALCULATION

Equation 18 is used to calculate the mass flux:

$$J_i = B \times v \left[\frac{mg}{s \times m^2} \right] \quad (18)$$

But B needs to be known, which can be obtained using equation 21

$$B = 427.3 - \left(\frac{-4,890.65 \times 2.66 \times 10^{-5}}{2.66 \times 10^{-7}} \right)$$

$$B = 489,492$$

Replacing B by the value in equation 18:

$$J_i = 489,492 \times 2.66 \times 10^{-7} \left[\frac{mg}{s \times m^2} \right]$$

$$J_i = 0.130 \left[\frac{mg}{s \times m^2} \right]$$

Comparing with the linear solution using equation 17 and its relative error:

Table 5. Results

	Measurement 1	Measurement 2	Measurement 3
Mass flux $\left[\frac{mg}{s \times m^2}\right]$	0.130 $\left[\frac{mg}{s \times m^2}\right]$	1.47 $\left[\frac{mg}{s \times m^2}\right]$	2.22 $\left[\frac{mg}{s \times m^2}\right]$
Mass flux $\left[\frac{mg}{s \times m^2}\right]$ (Solution for $v = 0$)	0.129 $\left[\frac{mg}{s \times m^2}\right]$	1.47 $\left[\frac{mg}{s \times m^2}\right]$	1.879 $\left[\frac{mg}{s \times m^2}\right]$
Error	< 1 %	< 1 %	15 %

7.4. RESOLUTION OF THE TYPE OF TRANSPORT OF MATTER

For the determination of the type of transport of matter in the measuring system, that is, if it is diffusive or advective-diffusive, the parameter N of equation 15 is used, evaluated for the different speeds obtained from Table 4:

$N \gg 1$ there is no mass flux.

$N > 1$ is only diffusive.

$N = 1$ advective-diffusive transition.

$0 < N < 1$ is advective-diffusive.

$$\text{Note: } z = -1[m], D = 2.66 \times 10^{-5} \left[\frac{m^2}{s}\right]$$

Table 6. Results

Equation 15	Measurement 1	Measurement 2	Measurement 3
$N = -\frac{D}{10 \times v \times z}$	10	1	0.1
Type of transport of matter	Diffusive	Advective-diffusive transition	Advective-diffusive

As seen in the theoretical exercise the system at low velocities delivers the same values as Fick's first law calculation. At higher velocities, the system estimates the advective process and obtains the value of the mass flux as the sum of the diffusive and advective process.

8. CORRECTIONS

The corrections of the system measurements associated with the changes in the physical-chemical parameters are:

Corrections for the isotopic composition of the gas.

Corrections for atmospheric pressure variations (not covered in this document).

Wind effect corrections are associated with the design of the gas interchanger (not covered in this document).

8.1. Corrections by gas isotopic composition

The carbon isotopic composition of CO₂ gas is an important marker for determining its origin in a volcano. The degassing of CO₂ in the upper magma shows typical values of $\delta^{13}\text{C}(\text{CO}_2)$ from -9 ‰ to -4 ‰ (Camarda et al., 2007). These variations will have little effect in the measurement system being converted from ppm to ‰ (at the time of using the molecular weight of 44.01 of the CO₂). The reader could see that only hundredths could affect the molecular weight value, so the effect can be considered negligible if the

units are given in $\frac{mol}{s \times m^2}$. Studying the isotopic marker in the soil where the measurement will be made is more important than this small adjustment in the formulas to measure the mass flux.

9. COMPARISON BETWEEN MODELS

For practical purposes, the open chamber model (diffusion chimney) for $v = 0$ is compared due to the large numerical approximation of the results when the $+\infty \gg N > 1$ (without showing the errors) with the closed camera model (accumulation chamber) to see the differences between the measurement models.

Replacing equations 3 and 22 in equation 17, you get:

$$J_i(z, C) = 1.21787 \times 10^{-6} \times T^{0.75} \times (C_{PPM_a} - C_{PPM_0}) \left[\frac{mg}{s \times m^2} \right] \quad (23)$$

Where:

$J(z, C)$ is the CO₂ mass flux in $\frac{mg}{s \times m^2}$

CPPMa is the concentration in ppm of the meter located in the DC at a distance $z = z_a = -0.333$ meters.

CPPM0 is the atmospheric concentration in ppm.

T is the operating temperature in [°K].

As can be seen, the mathematical model depends on a constant 1.21787×10^{-6} that includes the diffusion coefficient D, the distance $z = -0.333$ meters, the molecular weight of CO₂, and other parameters that do not depend on any other variable. The dependent variable depends only on the temperature T and the concentration difference in ppm. In this model, the pressure P does not affect the model since replacing the equations is canceled.

For the model of the closed chamber (accumulation chamber), the following equation is used using a West Systems instrument with a LICOR LI-800 Non-dispersive infrared CO₂ detector (West Systems, 2012):

$$J(t, C) = \frac{P \times V (C_f - C_i)}{R \times T \times A \times t} = \frac{P \times V}{R \times T \times A \times 10^6} \times \frac{(C_f - C_i)}{t} \left[\frac{mol}{s \times m^2} \right]$$

Resemble equation 23 by adding molecular weight MwCO₂ and 103, which is the conversion factor from grams to milligrams to adjust units for analysis (without showing errors) and separating independent variable constants. The following equation is:

$$J(t, C) = \frac{P \times V (C_f - C_i)}{R \times T \times A \times t} = \frac{V \times Mw_{CO_2} \times 10^{-3}}{R \times A} \times \frac{P \times (C_f - C_i)}{T \times t} \left[\frac{mg}{s \times m^2} \right] \quad (24)$$

As it can be seen, the mathematical model depends on a constant Importar imagen, which are the gas constant R, chamber volume V, chamber area A, molecular weight MwCO₂ from the CO₂, and the value 10⁻³ which is the compiled conversion factor of grams to milligrams and times of ppm. The dependent variable depends on pressure P, temperature T, and concentration difference in ppm. The $C_f - C_i$ value is the difference of concentrations in time t.

This latter e

As it can be seen, the mathematical model depends on a constant $\frac{V \times Mw_{CO_2} \times 10^{-3}}{R \times A}$, which are the gas constant R, chamber volume V, chamber area A, molecular weight MwCO₂ from the CO₂, and the value 10⁻³ which is the compiled conversion factor of grams to milligrams and times of ppm. The dependent variable depends on pressure P, temperature T, and concentration difference in ppm. The $C_f - C_i$ value is the difference of concentrations in time t.

This latter equation 24 has more independent variables than equation 23. The interesting thing about this analysis is that the “open chamber” model in the diffuse state only needs to know the temperature and difference of ppm to calculate the mass flux. Many CO₂ sensors give this information, so the absolute

pressure sensor for this model range is unnecessary, because variable P is canceled out in the mathematical development.

Table 7. Comparison of models

System	Constants	Independent variables	Simplified model
Open chamber (Diffusion chamber(DC)) Note: $\Delta z = 0.333$ immersed in 1.21787×10^{-6} and $v = 0$	1.21787×10^{-6}	$T^{0.75} \times (C_{ppH_2} - C_{ppH_0})$	$K_{CD} \times \frac{\Delta C}{\Delta z} \left[\frac{mg}{s \times m^2} \right]$
Closed chamber (Accumulation chamber (AC))	$\frac{V \times MW_{CO_2} \times 10^{-3}}{R \times A}$	$\frac{P \times (C_i - C_e)}{T \times t}$	$K_{AC} \times \frac{\Delta C}{\Delta t} \left[\frac{mg}{s \times m^2} \right]$

10. TECHNICAL ASPECTS OF IMPLEMENTATION

The GI is the key to the system since it is the one that allows the edge of the DC to occur at the reference concentration given by the atmosphere. Some recommendations of the system are:

A strong wind should not influenced it. This is a theoretical assumption that must be tested in practice. For this purpose, the GI must have protection so that the wind does not generate turbulence on the DC and does not affect the diffusive process at the beginning of the system. The wind must be perpendicular to the diffusive axis in the worst-case scenario.

There should be external light wind for the system to work well since the model assumes the atmosphere must give a concentration reference.

The area ratio between GI and DC should be at least 100, as a transition of the flux area of a magnitude of two orders reduces the maximum probable speed from $10^{-4} \frac{m}{s}$ to $10^{-6} \frac{m}{s}$, causing the GI to function under a diffusive regime. This allows for equalizing the external environmental concentration in the GI as a more precise measure of the CO₂ flux.

The sensitivity and response time of the system to CO₂ depends on:

The resolution of the NDIR detector of CO₂.

The volume ratio of DC and GI.

The length of the DC.

The ability of GI to mix gases without being affected by external wind turbulence.

11. ANALYTIC SOLUTION

11.1. Calculation of advective-diffusive mass flux

To obtain the mass flux equations, we start with the approach of equations 16.1, 16.2, and 16.3. From equation 18, it is observed that in order to calculate the mass flux, the constant B must be calculated first, and for this, equation 16.1 is used:

$$C(z = z_0 = 0) = A \frac{D}{v} + B = C_0 \quad (16.1)$$

Where B will be:

$$B = C_0 - A \frac{D}{v}$$

As can be seen, B depends on A, and to calculate it, we use 16.2 and 16.3, replacing each one with the previous equation.

Replacing the previous equation in 16.2 and 16.3, respectively, and obtaining A:

$$A = \frac{v}{D} \times \frac{(C_a - C_0)}{e^{\frac{v}{D} z_a} - 1} \quad (21.1)$$

$$A = \frac{v}{D} \times \frac{(C_b - C_0)}{e^{\frac{v}{D} z_b} - 1} \quad (21.2)$$

Equation 21.1 and equation 21.2 are equalized so that only v is unknown:

$$A = \frac{(C_b - C_0)}{e^{\frac{v}{D} z_b} - 1} = \frac{(C_a - C_0)}{e^{\frac{v}{D} z_a} - 1}$$

Solving:

$$(e^{\frac{v}{D} z_b} - 1) (C_a - C_0) = (C_b - C_0) (e^{\frac{v}{D} z_a} - 1)$$

For practical purposes the following replacement is made $CC_b = C_b - C_0$, $CC_a = C_a - C_0$:

$$e^{\frac{v}{D} z_b} CC_a - e^{\frac{v}{D} z_a} CC_b + CC_b - CC_a = 0 \quad (25)$$

The solution to this equation has two parts, the quadratic solution when the sensor is in the middle of the DC and the cubic solution when the sensor is in the third part of the DC. The following substitution is performed for the solution:

To solve in a quadratic way, it is necessary to execute $z_b = 2 \times z_a$.

To solve in the cubic form, it is necessary to execute $z_b = 3 \times z_a$.

11.1.1. Mathematical solution (Quadratic)

The variables to be used are A, B, and v . To obtain B, equation 25 is used, substituting $z_b = 2 \times z_a$:

$$e^{\frac{v}{D} 2z_a} CC_a - e^{\frac{v}{D} z_a} CC_b + CC_b - CC_a = 0$$

A variable change is made $Y = e^{\frac{v}{D}}$:

$$Y^2 CC_a - Y CC_b + (CC_b - CC_a) = 0$$

the quadratic equation solution is applied:

$$a = CC_a, b = -CC_b, c = CC_b - CC_a$$

$$Y = \frac{-(b) \pm \sqrt{b^2 - 4ac}}{2a}$$

$$Y = \frac{-(-CC_b) \pm \sqrt{(-CC_b)^2 - 4CC_a(CC_b - CC_a)}}{2CC_a}$$

The next solutions are obtained:

$$Y_1 = 1$$

$$Y_2 = \text{Valid solution}$$

Changing the variable, the velocity is obtained depending on C₀, C_a, C_b, D, and z_a.

$$v = \frac{\ln(Y_2) D}{z_a}$$

This solution Y₂ will not be practical, but the solution Y₁ = 1 will be useful for the other solution by applying the substitution z_b = 3 × z_a.

11.1.2. Mathematical solution (Cubic)

The cubic solution is developed in the same way as the quadratic solution until equation 25 is obtained:

$$e^{\frac{v}{D} z_b} C C_a - e^{\frac{v}{D} z_a} C C_b + C C_b - C C_a = 0 \quad (25)$$

Replacing z_b = 3 × z_a, and doing Y = e ^{$\frac{v}{D} z_a$} :

$$Y^3 C C_a - Y C C_b + (C C_b - C C_a) = 0$$

It is divided by C C_a

$$Y^3 - Y \frac{C C_b}{C C_a} + \frac{(C C_b - C C_a)}{C C_a} = 0$$

Which is a cubic equation of the form:

$$a_2 Y^3 + b_2 Y^2 + c_2 Y + d_2 = 0$$

In order to solve the cubic equation, the solution form will have the form (Y – Y₁)(Y – Y₂)(Y – Y₃) whose solutions are matching term to term:

$$Y_1 + Y_2 + Y_3 = -\frac{b_2}{a_2} \quad (26)$$

$$Y_1 Y_2 + Y_1 Y_3 + Y_2 Y_3 = \frac{c_2}{a_2} \quad (27)$$

$$Y_1 Y_2 Y_3 = -\frac{d_2}{a_2} \quad (28)$$

As it is known from the previous quadratic solution that Y₁ = 1 which replaced in equations 26, 27, and 28, and, in addition, it is also known that a₂ = 1 and b₂ = 0.

$$1) 1 + Y_2 + Y_3 = 0 \Rightarrow Y_2 = -1 - Y_3$$

$$2) Y_2 + Y_3 + Y_2 Y_3 = c_2$$

$$3) Y_2 Y_3 = -d_2$$

Since there are only two unknowns and three equations, only two equations are enough to solve the problem since one of the equations is linearly dependent on another. Therefore, Y_2 is obtained from the first and replaced in the second.

$$\begin{aligned} -1 - Y_3 + Y_3 + (-1 - Y_3)Y_3 &= c_2 \\ -1 - Y_3 - Y_3^2 &= c_2 \end{aligned}$$

Organizing:

$$Y_3^2 + Y_3 + 1 + c_2 = 0 \quad (29)$$

Which is again a quadratic equation with the following coefficients:

$$a_3 = 1, b_3 = 1, c_3 = 1 + c_2$$

Where Y_3 has a quadratic solution:

$$\begin{aligned} Y_3 &= \frac{-(b_3) \pm \sqrt{b_3^2 - 4a_3c_3}}{2a_3} \\ Y_3 &= \frac{-(1) \pm \sqrt{(1)^2 - 4(1 + c_2)}}{2(1)} \end{aligned}$$

When replacing $c = \frac{C_b}{C_a}$, the next result is obtained:

$$Y_3 = \frac{-1 \pm \sqrt{1 - 4 \times \left(1 - \frac{(C_b - C_0)}{(C_a - C_0)}\right)}}{2}$$

The solution with the positive (+) sign is taken since the negative solution is a physically not possible solution for this model:

$$Y = \frac{-1 + \sqrt{1 - 4 \times \left(1 - \frac{(C_b - C_0)}{(C_a - C_0)}\right)}}{2} \quad (20)$$

Changing the variable again, the velocity is obtained in the function of C_0 , C_a , C_b , D and z_a :

$$v = \frac{\ln(Y) \times D}{z_a} \quad (19)$$

12. CONCLUSIONS

A stations network implementing the newly proposed technique would be possible to establish a continuous measurement of CO_2 per day emitted at a specific area of a volcano, and it could be validated with non-continuous and non-telemetric measurements, for instance, using the manual accumulation chamber portable instrument.

The solution of a 3×3 equations system using data from NDIR sensors and other parameters does not require knowledge of the soil characteristics that condition the speed of the gas that emerges due to advection-diffusion.

A new parameter in this paper called N will establish the state of the measurement system in a simplified way, defining the diffusive or advective-diffusive state and the inflection point.

The new element, called a gas interchanger, is key to the measurement system to avoid affectation by wind and external dust.

Any NDIR with a resolution of 10 ppm has sufficient capacity to measure a mass flow and the resolution is also determined by the gas interchanger that sets the external reference. Therefore, mathematically it can be verified that 10 ppm error generates approximately 1 % theoretical error in measuring the mass flux.

For the solution of the system of equations, it is necessary to have the environmental concentration of CO₂. The momentary agitation of the gas could obtain this value with an agitation fan in the diffusion chimney and the gas interchanger. The atmospheric concentration will be reported simultaneously by NDIR sensors at the time of shutting down the fan.

It is necessary to use an embedded system to determine the CO₂ mass flux from the volcano, using a good arrangement of the concentration, temperature, and pressure sensors in the tubes, controlling an agitation fan, and processing data remotely or locally. One difference with open chamber assemblies is that the inclusion of the gas interchanger is proposed here.

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REFERENCES

- Allard P., Carbonnelle J., Dajlevic D., Le Bronec J., Morel P., Robe M. C., Maurenas J. M., Faivre-Pierret R., Martin D., Sabroux J. C., & Zettwoog P. (1991). Eruptive and diffuse emission of CO₂ from Mount Etna. *Nature*, 351, 387-391. <https://doi.org/10.1038/351387a0>
- Badalamenti, B., Gurrieri, S., Hauser, S., & Valenza, M. (1988). Ground CO₂ output in the island of Vulcano during the period 1984-1988: Gas hazard and volcanic activity surveillance implications. *Rend. Società Italiana di Mineralogia e Petrologia*, 43, 893-899.
- Baubron, J. C., Allard, P., & Toutain, J. P. (1990). Diffuse volcanic emissions of carbon dioxide from Vulcano island, Italy. *Nature*, 344, 51-53. <https://doi.org/10.1038/344051a0>
- Badalamenti, B., Gurrieri, S., Nuccio, P. M., & Valenza, M. (1991). Gas hazard on Vulcano Island. *Nature*, 350, 26-27.
- Bekku, Y., Koizumi, H., Nakadai, T., & Iwaki, H. (1955). Measurement of soil respiration using close chamber method: An IRGA technique. *Ecological Research*, 10(3), 369-373. <https://doi.org/10.1007/BF02347863>
- Busquets D. (2011). Difusión: 2º ley de Fick. Universidad Politécnica de Valencia. www.youtube.com/watch?v=HHBvZDNvTic
- Camarda, M., De Gregorio, S., Favara, R., & Gurrieri, S. (2007). Evaluation of carbon isotope fractionation of soil CO₂ under an advective-diffusive regimen: A tool for computing the isotopic composition of unfractionated deep source. *Geochimica et Cosmochimica Acta*, 71(12), 3016-3027. <https://doi.org/10.1016/j.gca.2007.04.002>

- Camarda, M., Gurrieri, S., & Valenza, M. (2006). CO₂ flux measurements in volcanic areas using the dynamic concentration method: Influence of soil permeability. *Journal of Geophysical Research: Solid Earth*, 111(B5), B05202. <https://doi.org/10.1029/2005JB003898>
- Campbell, G. S. (1985). *Soil physics with basic transport models for soil-plant systems*. Elsevier.
- Callister W. D. (1995). *Introducción a la Ciencia e Ingeniería de los materiales*. Reverte.
- Cardellini, C., Chiodini, G., & Frondini, F. (2003). Application of stochastic simulation to CO₂ flux from soil: Mapping and quantification of gas release. *Journal of Geophysical Research. Solid Earth*, 108(B9), 2425.
- Chiodini, G., & Frondini, F. (2001). Carbon dioxide degassing from the Albani Hills volcanic region, Central Italy. *Chemical Geology*, 177(1-2), 67-83. [https://doi.org/10.1016/S0009-2541\(00\)00382-X](https://doi.org/10.1016/S0009-2541(00)00382-X)
- Chiodini, G., Cioni, R., Guidi, M., Raco, B., & Marini, L. (1998). Soil CO₂ flux measurements in volcanic and geothermal areas. *Applied Geochemistry*, 13(5), 543-552. [https://doi.org/10.1016/S0883-2927\(97\)00076-0](https://doi.org/10.1016/S0883-2927(97)00076-0)
- Ciotoli, G., Guerra, M., Lombardi, S., & Vittori, E. (1998). Soil gas survey for tracing seismogenic faults: A case-study in the Fucino basin (central Italy). *Journal of Geophysical Research*, 103(B10), 23 781-23 794. <https://doi.org/10.1029/98JB01553>
- Ciotoli, G., Della Seta, M., Del Monte, M., Fredi, P., Lombardi, S., Palmieri, E. L., & Pugliese, F. (2003). Morphological and geochemical evidence of neotectonics in the volcanic area of Monti Vulsini (Latium, Italy). *Quaternary International*, 101-102, 103-113. [https://doi.org/10.1016/S1040-6182\(02\)00093-9](https://doi.org/10.1016/S1040-6182(02)00093-9)
- Cropper Jr., W. P., Ewel K. C., & Raich, J. W. (1985). The measurement of soil CO₂ evolution in situ. *Pedobiologia* 28, 35-40.
- Diliberto, I. S., Gurrieri, S., & Valenza, M. (1993). Vulcano: Gas geochemistry. CO₂ flux from the ground. *Acta Vulcanologica*, 3, 272-273.
- García, I. (2020). *Fenómenos de transporte y conductividad electrolítica*. Universidad de Valencia.
- Gerlach, T. M., Doukas, M. P., McGee, K. A., & R. Kessler. (2001). Soil efflux and total emission rates of magmatic CO₂ at the Horseshoe Lake tree kill, Mammoth Mountain, California, 1995-1999. *Chemical Geology*, 177(1-2), 101-116. [https://doi.org/10.1016/S0009-2541\(00\)00385-5](https://doi.org/10.1016/S0009-2541(00)00385-5)
- Giammanco, S., Gurrieri, S., & Valenza, M. (1995). Soil CO₂ degassing on Mt. Etna (Sicily) during the period 1989-1993: Discrimination between climatic and volcanic influences. *Bulletin of Volcanology*, 57, 52-60. <http://doi.org/10.1007/BF00298707>
- Giammanco S., Gurrieri, S., & Valenza, M. (1998). Anomalous soil CO₂ degassing in relation to faults and eruptive fissures on Mount Etna (Sicily, Italy). *Bulletin of Volcanology*, 60, 252-259. <https://doi.org/10.1007/s004450050231>
- Guerra, M., & Lombardi, S. (2001). Soil-gas method for tracing neotectonic faults in clay basins: The Pisticci field (southern Italy). *Tectonophysics*, 339(3-4), 511-522. [https://doi.org/10.1016/S0040-1951\(01\)00072-5](https://doi.org/10.1016/S0040-1951(01)00072-5)
- Gurrieri, S., & Valenza, M. (1988). Gas transport in natural porous medium: a method for measuring soil CO₂ flows from the ground in volcanic and geothermal areas. *Rendiconti della Società Italiana di Mineralogia e Petrologia*, 43, 1151-1158.
- Hernández, P., Notsu, K., Salazar, J., Mori, T., Natale, G., Okada, H., Virgili, G., Shimoike, Y., Sato, M., & Pérez, N. (2001). Carbon dioxide degassing by advective flow from Usu Volcano, Japan. *Science*, 292(5514): 83-86. <http://doi.org/10.1126/science.1058450>
- Inguaggiato, S., Jácome Paz, M. P., Mazot, A., Delgado Granados, H., Inguaggiato, C., & Vita, F. (2013). CO₂ output discharged from Stromboli Island (Italy). *Chemical Geology*, 339, 52-60. <https://doi.org/10.1016/j.chemgeo.2012.10.008>
- Isachenko V., Osipova V., & Sukomel A. (1980). *Heat Transfer*. Mir Publisher.
- Jácome Paz, M. P., Taran, Y., Inguaggiato, S., & Collard, N. (2016). CO₂ flux and chemistry of El Chichón Crater Lake (México) in the period 2013-2015: Evidence for the enhanced volcano activity. *Geophysical Research Letters*, 43(1), 27-134. <https://doi.org/10.1002/2015GL066354>

- Janssens, I., Kowalski, A., Longdoz, B., & Ceulemans, R. (2000). Assessing forest soil CO₂ efflux: an in-situ comparison of four techniques. *Tree Physiology*, 20(1), 23-32. <https://doi.org/10.1093/treephys/20.1.23>
- Hernández, P. A., Salazar, J. M., Shimoike, Y., Mori, T., Notsu, K., & Pérez, N. M. (2001). Diffuse emission of CO₂ from Miyakejima volcano, Japan. *Chemical Geology*, 177(1-2), 175-185. [https://doi.org/10.1016/S0009-2541\(00\)00390-9](https://doi.org/10.1016/S0009-2541(00)00390-9)
- Moreno, J. (2005). Metodología para el cálculo de incertidumbre. Encuentro Nacional de metrología eléctrica, México.
- Nakadai, T., Koizumi, H., Usami, Y., Satoh, M., & Oikawa, T. (1993). Examination of the method for measuring soil respiration in cultivated land: Effect of carbon dioxide concentration on soil respiration. *Ecological Research*, 8(1), 65-71. <https://doi.org/10.1007/BF02348608>
- Norman, J. M., García, R., & Verma, S. B. (1992). Soil surface CO₂ fluxes and the carbon budget of a grassland. *Journal of Geophysical Research: Atmospheres*, 97(D17), 18 845-18 853. <https://doi.org/10.1029/92JD01348>
- Notsu, K., Mori, T., Chanchah, D., Vale, S., Kagi, H., & Ito, T. (2006). Monitoring quiescent volcanoes by diffuse CO₂ degassing: case study of Mt. Fuji, Japan. *Pure and Applied Geophysics*, 163(4), 825-835. <https://doi.org/10.1007/s00024-006-0051-0>
- Rogie, J. D., Kerrick, D. M., Sorey, G., Chiodini, M. L., & Galloway, D. L. (2001). Dynamics of carbon dioxide emission at Mammoth Mountain Continuous monitoring of diffuse CO₂ degassing, Horseshoe Lake, Mammoth Mountain, California. *Earth and Planetary Science Letters*, 188(3-4), 531-541. [https://doi.org/10.1016/S0012-821X\(01\)00344-2](https://doi.org/10.1016/S0012-821X(01)00344-2)
- Sahimi, M. (1995). Flow and Transport in Porous Media and Fractured Rock: From Classical Methods to Modern Approaches. Wiley-VCH Verlag GmbH & Co. <https://doi.org/10.1002/9783527636693>
- Salazar, J. M. L., Pérez, N. M., Hernández, P. A., Soriano, T., Barahona, F., Olmos, R., Cartagena, R., López, D. L., Lima, R. N., Melián, G., Galindo, I., Padrón, E., Sumino, H., & Notsu, K. (2002). Precursory diffuse carbon dioxide degassing signature related to a 5.1 magnitude earthquake in El Salvador, Central America. *Earth and Planetary Science Letters*, 205(1-2), 81-89. [https://doi.org/10.1016/S0012-821X\(02\)01014-2](https://doi.org/10.1016/S0012-821X(02)01014-2)
- Spicák, A., & Horálek, J. (2001). Possible role of fluids in the process of earthquakes swarm generation in the West Bohemia/Vogtland seismoactive region. *Tectonophysics*, 336(1-4), 151-161. [https://doi.org/10.1016/S0040-1951\(01\)00099-3](https://doi.org/10.1016/S0040-1951(01)00099-3)
- Tonani, F., & Miele, G. (1991). Methods for measuring flow of carbon dioxide through soils in the volcanic setting. International Conference Active Volcanoes and Risk Mitigation, IAVCEI, Naples, Italy.
- Wakita, H. (1996). Geochemical challenge to earthquake prediction. *PNAS*, 93(9), 3781-3786. <https://doi.org/10.1073/pnas.93.9.3781>
- West Systems. (2012). Portable difusse flux meter with LI-COR CO₂ detector. HandBook.
- Witkamp, M. (1966). Decomposition of leaf litter in relation to environment, microflora and microbial respiration. *Ecology*, 47(2), 194-201. <https://doi.org/10.2307/1933765>
- World Meteorological Organization (WMO). (2019). The State of Greenhouse Gases in the Atmosphere Based on Global Observations through 2018. WMO Greenhouse Gas Bulletin, (15).